

VI.

ATMOSPHERIC PERSISTENCE

Among other factors, the combustibility of tobacco components, insufficient supply of oxygen, and the existence of a temperature gradient in the burning cone, makes ETS a mixture of several thousand compounds. Due to the complex chemical nature of ETS, a discussion of the atmospheric persistence of the “mix” as a whole is not practical. However, there are data on the atmospheric reactions that occur to several groups of ETS-related chemicals. Therefore, in this chapter we provide a general discussion of what is known about the atmospheric persistence of chemical groups within ETS, including nicotine, N-Nitrosamines and PAHs.

Studies show that the combustion of cigarettes include at least three important types of reactions, including: pyrolysis, pyrosynthesis, and distillation (NIH, 1998). The result of these reactions is the production of thousands of gaseous and particle constituents. Eventually, this complex mixture undergoes additional chemical reactions as the mix is diluted with ambient air, yielding individual compounds with their own atmospheric lifetimes. According to the Morawska *et al.* (1997) chamber and indoor environment study, the lifetime of the mixture of ETS constituents in the air may be up to several hours depending on the air ventilation rate, humidity, and atmospheric conditions.

A. ATMOSPHERIC REACTIONS OF GASEOUS SPECIES

Gaseous ETS constituents can react in the atmosphere with other pollutants and sunlight to form new chemical species (see Table III-2 in Chapter III for a list of gaseous components found in ETS; Appendix A contains a comprehensive list). For example, 1,3-butadiene can initially react in the atmosphere with the hydroxyl radical (OH), nitrate radical (NO₃), and ozone (O₃) to form acrolein and formaldehyde (Atkinson, 1994; Skov *et al.*, 1992). Gaseous species may also transform into particle phase species. For example, gas phase ammonia can react with gaseous nitric acid to form particulate ammonium nitrate (Atkinson, 1995). Exposure to ammonium nitrate has been found to cause burning or irritation of eye and skin (ARB, 1997a). Alternatively, as ETS ages, semi-volatile constituents of ETS, such as nicotine and neophytadiene, may shift from particulate phase to the gaseous phase.

Gaseous ETS components primarily react with the following:

- Sunlight through photolysis
- O₃ (ozone)
- OH radical during the daylight hours
- NO₃ radical during the nighttime hours
- Gaseous nitric acid (HNO₃)
- Nitrogen dioxide (NO₂)

- Hydroperoxy radical (HO_2) mainly during afternoon/evening hours

Important reaction processes for most gas-phase organic compounds are photolysis and subsequent reaction with O_3 , as well as the OH and NO_3 radicals. For a few compounds, one or more of the other reactive chemical species (HO_2 , NO_2 , and/or HNO_3) may react at significant rates. For example, HO_2 radicals react with formaldehyde, acetaldehyde, and glyoxal, NO_2 reacts with conjugated dienes, and gaseous HNO_3 reacts with the amines. Table VI-1 provides examples of the atmospheric lifetimes and the dominant removal processes for some of the gaseous species found in ETS.

Table VI-1

**Estimated Atmospheric Lifetimes
of Selected ETS Constituents**

	Dominant Removal Process	Atmospheric Lifetime
Formaldehyde	Photolysis	4 hours
1,3 Butadiene	OH radical	1-9 hours (half-life)
Acetaldehyde	OH radical	22 hours
Acrolein	OH radical	17 hours
Benzene	OH radical	12 days
N-Nitrosodimethylamine	Photolysis	5 minutes
Toluene	OH radical	2.4 days
PAHs (gas phase)	OH radical	3-27 hours

Source: ARB, 1998.

Gaseous species absorbed by particles may be unavailable for further chemical reaction. Gaseous species adsorbed to particles may be degraded by photolysis and reaction with atmospheric O_3 , dinitrogen pentoxide (N_2O_5), NO_2 , HNO_3 , nitrous acid (HNO_2), sulfuric acid (H_2SO_4), and hydrogen peroxide (H_2O_2).

B. ATMOSPHERIC REACTIONS OF PARTICULATE SPECIES

Particles in the range of 0.01-10 μm are often referred to as respirable suspended particles (RSP). Typically, all of the ETS associated particles fall in the range of between 0.01 and 1.0 μm (U.S. EPA, 1992). ETS contains particulate species which have their own atmospheric persistence rates based on the particle size. The two most important processes affecting particle ETS species in the atmosphere are:

- Dry and wet deposition (i.e., physical removal) of particles, and
- Atmospheric transformations of species adsorbed to the particles.

Dry deposition is broadly defined as the transport of air pollutants from the atmosphere onto surfaces in the absence of precipitation (Davidson and Wu, 1989; Seinfeld and Pandis, 1998). Major factors affecting dry deposition are atmospheric turbulence,

chemical, and physical properties of the air pollutants and the nature of the depositing surface. Particles in the size range of 0.05 to 1 μm are expected to reside in the atmosphere for long time periods and can be transported over long distance (Cohen, 1998).

Virtually complete removal of particles in the range of 0.1 to 10 μm in diameter is expected by wet deposition (Leuenberger *et al.*, 1985, Ligoeki *et al.*, 1985 a,b). Since ETS particles are in this size range (0.1-1 μm), they are expected to be efficiently washed from the atmosphere by wet deposition. Wet deposition occurs due to events such as rain, cloud, fog, or snow.

C. NICOTINE

Nicotine is the principal alkaloid in tobacco and a major contributor to the addictive properties of tobacco. In ETS, studies report that nicotine is most commonly found in the gas phase within the environment (Eudy *et al.*, 1986; Thome *et al.*, 1986; Eatough *et al.*, 1986; Hammond *et al.*, 1987). Organic compounds with vapor pressure between 10^{-6} and 10 Pascals (Pa) at ambient temperatures are classified as semi-volatile organic compounds. At 298 °K, nicotine has a vapor pressure of 2.7 Pa and is almost entirely present in gas phase (Von Loy *et al.*, 2001). Less than five percent of ETS nicotine has been associated with the particulate phase (Jenkins *et al.*, 2000). Also, in sidestream smoke, the alkaline nature of ambient air leads to gas phase nicotine rather than in the particulate phase. Gas phase nicotine in ETS is expected to be removed from the environment at a faster rate than other ETS components (Eudy *et al.*, 1986; Eatough *et al.*, 1986). Therefore, measurements of all gas phase nicotine components in ETS may be difficult to obtain. (Eatough *et al.*, 1989). In ambient air, nicotine may react with photochemically generated hydroxyl radicals. The reported half-life of nicotine in the ambient atmosphere is approximately 1 day (Spectrum Chemical Fact Sheet, 2003).

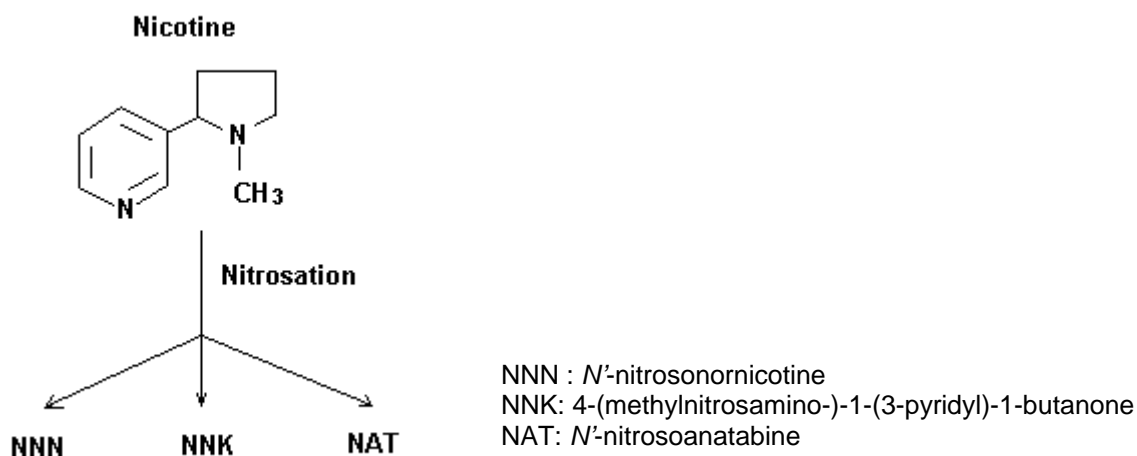
In indoor air, studies show that the nicotine level decreases rapidly as a consequence of sorptive uptake on different surrounding surfaces (Eatough *et al.*, 1986; Piade *et al.*, 1999; Von Loy *et al.*, 2001). Therefore, nicotine is a reasonable indicator of ETS exposures occurring within the previous few hours, with its indoor half-life of approximately two hours (Trinh and Huynh, 1989). Research also indicates that sorbed nicotine present on surrounding materials, such as walls and carpets, may be re-emitted to the environment over time (Trinh and Huynh, 1989). According to the Piade *et al.* (1999) study, as much as 1 mg of nicotine can be adsorbed and re-emitted from 1 m^2 of cotton cloth over a few hours. The Von Loy *et al.* (2001) chamber experiments also observed desorption of nicotine from surrounding materials. After flash evaporation of nicotine in a 20 m^3 environmental test chamber with a carpet floor covering (measured nicotine air concentration of 4.4 $\mu\text{g}/\text{m}^3$), the chamber was flushed with clean air for 3 days. After resealing the chamber, the nicotine concentration slowly rose back to 1 $\mu\text{g}/\text{m}^3$, which demonstrates the effect of nicotine being re-emitted from surrounding material surfaces.

D. TOBACCO-SPECIFIC N-NITROSAMINES

While nicotine has not been identified as a carcinogen, several tobacco-specific nitrosamines (TSNAs), which are derived from nicotine and other tobacco alkaloids, may be carcinogenic (Hecht and Hoffmann, 1988). TSNAs (see Figure VI-1) are formed by N-nitrosation of nicotine during the curing, processing, fermentation, and combustion of tobacco products (IARC 1986; Ashley *et al.*, 2003). The yield of TSNA from smoking depends on the nitrate content of tobacco. Certain flue-cured tobaccos exposed to NO_x during the curing process contain higher levels of TSNAs (Ashley *et al.*, 2003).

Figure VI-1

Nicotine Conversion



N'-nitrosoornicotine (NNN) and 4-(methylnitrosamino)-1-(3-pyridyl)-1-butanone (NNK) are believed to be the most potent carcinogens of the TSNA class (Ashley *et al.*, 2003).

N-nitroso compounds are degraded in the presence of ultraviolet and visible light. When heated to decomposition, these compounds emit toxic fumes of nitrogen oxides (NTP, 2002).

E. PAH AND PAH-DERIVATIVES

Researchers have identified at least ten polycyclic aromatic hydrocarbon (PAH) isomers in ETS, which have been identified as cancer causing toxic air contaminants (Hoffmann and Hoffmann, 1997; OEHHA, 1997). Some PAHs react with NO_x emissions in the atmosphere to mutate to form nitro-derivative PAHs (ARB, 1994). Both gas and particle phase PAHs have been measured in ETS (Gundel *et al.*, 1995). Table VI-2

shows a list of identified gaseous and particulate PAHs that have been identified in ETS.

Table VI-2

PAHs Detected in ETS

Gas-Phase PAHs	Particle-Phase PAHs
1-methylnaphthalene	1,2-benzofluorene
2-methylnaphthalene	Anthracene
Anthracene	Benz[a]anthracene
Benz[a]anthracene	Benzo[a]pyrene
Chrysene	Benzo[b]fluoranthene
Fluoranthene	Benzo[k]fluoranthene
Fluorene	Chrysene
Naphthalene	Fluoranthene
Phenanthrene	Phenanthrene
Pyrene	Pyrene
	Triphenylene

Source: Gundel *et al.*, 1995.

One of the most potent cancer-causing PAHs in ETS is benzo[a]pyrene. Benzo[a]pyrene exists almost entirely in the particle phase in the atmosphere with a size of three μm or less and, therefore, subject to wet and dry deposition (ARB, 1997b). The average half-life of particle benzo[a]pyrene in the atmosphere is estimated to be about 3.5 to 10 days and lifetime of 5 to 15 days (ARB, 1997b). Other lifetimes of PAHs are shown in Table VI-3.

Table VI-3

**Estimated Atmospheric Lifetimes
of Selected PAHs**

PAHs in ETS	Lifetime due to reaction with:		
	OH ^{a/}	NO ₃ ^{b/}	O ₃ ^{c/}
1- methylnaphthalene	3.5 hrs	50 days	>125 days
2-methylnaphthalene	3.6 hrs	40 days	>40 days
Anthracene	1.4 hrs		
Fluoranthene	~3.7 hrs ^{d/}	~85 days	
Pyrene	~3.7 hrs ^{d/}	~30 days	

Source: ARB, 1998.

^{a/} For a 12-hr daytime average OH radical concentration of 1.5×10^6 molecule cm^{-3} (Prinn *et al.*, 1987).

^{b/} For a 12-hr average nighttime NO₃ radical concentration of 2.4×10^8 molecule cm^{-3} and an NO₂ concentration of 2.4×10^{12} molecule cm^{-3} (Atkinson *et al.*, 1986).

- c/ For a 24 hr average O₃ concentration of 7×10^{11} molecule cm⁻³ (Logan, 1985).
d/ Using estimated OH radical reaction rate constant correlation with ionization potential (Biermann *et al.*, 1985; Arey *et al.*, 1990; Atkinson *et al.*, 1990).

Volatile, 2- to 4-ring PAHs exist in the atmosphere mostly in the gas phase (Atkinson and Arey, 1994). The gas-phase PAHs react with hydroxyl (OH) radicals, NO₃ radicals, and ozone in the atmosphere, with the OH radical reaction generally dominating as the PAHs loss process (Atkinson and Arey, 1994). The products of the OH radical reactions with PAHs include formation of hydroxyl-PAH, nitro-PAH, and ring-opened dicarbonyls (ARB, 1997b). The estimated half-life of the gas phase 2- and 4-ring volatile PAHs in the atmosphere due to reaction with the OH radical are in the range of 2 to 19 hours and have a lifetime of 3 to 27 hours, (Atkinson and Arey, 1994).

REFERENCES

- ARB, (1994). *Benzo[a]pyrene as a Toxic Air Contaminant*. Staff Report. Executive Summary, California Air Resources Board.
- ARB, (1997a). California Air Resources Board. *Toxic Air Contaminant Identification List Summaries, Ammonium Nitrate*. pp.55.
- ARB, (1997b). California Air Resources Board. *Toxic Air Contaminant Identification List Summaries, Polycyclic Organic Matter*. pp. 803.
- ARB, (1998). California Air Resources Board. *Proposed Identification of Diesel Exhaust as a Toxic Air Contaminant. Part A. Exposure Assessment*. pp. A-71.
- Arey J., Atkinson R., Aschmann S.M., Schuetzle D. (1990). *Experimental Investigation of the Atmospheric Chemistry of 2-Methyl-1-nitronaphthalene and a Comparison of Predicted Nitroarene Concentrations with Ambient Air Data*. Polycyclic Aromat. Compounds. Vol. 1, pp.33-50.
- Ashley D.L., Beeson M.D., Johnson D.R., McCraw J.M., Richter P., Pirkel J.L., Oechacek T.F., Song S., Watson C.H. (2003). *Tobacco-Specific nitrosamines in tobacco from U.S. brand and non-U.S. brand cigarettes*. Nicotine & Tobacco Research. Vol 5, pp. 323-331.
- Atkinson R. (1994). *Gas-phase tropospheric chemistry of organic compounds*. J. Phys. Chem. Ref. Data. Monograph 2. pp.1-216.
- Atkinson R., Arey J. (1994). *Atmospheric chemistry of gas-phase polycyclic aromatic hydrocarbons: Formation of atmospheric mutagens*. Environ. Health Perspect. Vol. 102 (Suppl. 4), pp.117-126.
- Atkinson R. (1995). Personal review of the Air Resources Board's Toxic Air Contaminant Identification List compounds. University of California, Riverside.
- Atkinson R. (1986). *Kinetics and Mechanisms of the Gas-phase Reactions of the Hydroxyl Radical with Organic Compounds under Atmospheric Conditions*. Chem. Rev. Vol. 86, pp. 69-201.
- Atkinson R. (1990). *Gas-phase Tropospheric Chemistry of Organic Compounds: a Review*. Atmos. Environ. Vol. 24A, pp. 1-41.
- Biermann H.W., Mar Leod H., Atkinson R., Winer A.M., Pitts Jr. J.N. (1985). *Kinetics of the Gas-phase Reactions of the Hydroxyl Radical with Naphthalene, Phenanthrene, and Anthracene*. Environ. Sci. Technol. Vol. 19, pp. 244-248.

Cohen Y. (1998). *Environmental Multimedia Transportation Phenomena*. Chapter 11. Department of Chemical Engineering. University of California, Los Angeles. Multimedia Envirosoft Corporation.

Davidson C.I. and Wu Y.L. (1989). "*Dry Deposition of Trace Elements*," in *Control and Fate of Atmospheric Heavy Metals*, J.M. Pacyna and B. Ottar, editors, NATO ASI Series, Series C, Volume 268, Kluwer Academic Publishers, Dordrecht. pp. 147-202.

Eatough D.J., Benner C., Mooney R.L., Bartholomew D., Steiner D.S., Hansen L.D., Lamb J.D., Lewis E.A. (1986). *Gas and particle phase nicotine in environmental tobacco smoke*. Proceedings, 79th Annual Meeting of the Air Pollution Control Association. Paper 86-68.5, Pittsburgh, PA.

Eatough E.J., Benner C.L., Tang H., Landon V., Richards G. (1989). *The Chemical Composition of Environmental Tobacco Smoke. III. Identification of Conservative Tracers on Environmental Tobacco Smoke*. Environmental International. Vol. 15, pp. 19-28.

Eudy L.W., Thorne F.W., Heavner D.K., Green C.R., Ingebrethsen B.J. (1986). *Studies on the vapor-particulate phase distribution of environmental nicotine by selective trapping and detection methods*. Proceedings, 79th Annual Meeting of the Air Pollution Control Association. Paper 86-38.7, Pittsburgh, PA.

Gundel L.A., Mahanama K.R.R., Daisy J.M. (1995). *Semivolatile and Particulate Polycyclic Aromatic Hydrocarbons in Environmental Tobacco Smoke: Cleanup, Speciation, and Emission Factors*. Environ. Sci. Technol. Vol. 29, pp. 1607-1614.

Hammond S.K., Leaderer B.P., Roche A.C., Scjemker M. (1987). *Collection and Analysis of Nicotine as a Marker for Environmental Tobacco Smoke*. Atmospheric Environment. Vol. 21, No. 2, pp. 457-462.

Hecht S.S., Hoffmann D. (1988). *Tobacco-specific nitrosamines, an important group of carcinogens in tobacco and tobacco smoke*. Carcinogenesis. Vol. 9, pp. 875-884.

Hoffmann D., Hoffmann I. (1997). *The changing cigarette, 1950-1995*. Journal of Toxicology and Environmental Health. Vol. 50(4), pp.307-364.

IARC, (1986). International Agency for Research on Cancer *IARC Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Humans*. Tobacco Smoking. Vol. 38. pp.110-114. Lyon, France: IARC.

Jenkins R.A., Guerin M.R., Tomkins B.A. (2000). *The Chemistry of Environmental Tobacco Smoke: Composition and Measurement*. Lewis Publishers. Chelsea, Michigan.

Leuenberger D., Ligocki M.P., Pankow J.F. (1985). *Trace organic compounds in rain. 4.Identities, concentrations and scavenging mechanisms for phenols in urban air and rain.* Environ. Sci. Technol. Vol. 19, pp. 1053-1058.

Ligocki M.P., Leuenberger C., Pankow J.F. (1985a). *Trace organic compounds in rain – III. Particle scavenging of neutral organic compounds.* Atmos. Environ. Vol. 19, pp. 1619-1626.

Ligocki M.P., Leuenberger C., Pankow J.F. (1985b). *Trace organic compounds in rain – II. Particle scavenging of neutral organic compounds.* Atmos. Environment. Vol. 19, pp. 1609-1617.

Logan J.A. (1985). *Tropospheric ozone: seasonal behavior, trends, and anthropogenic influence.* J. Geophys. Res. Vol. 90, pp. 10463-10482.

Morawska L., Jamriska M., Bofinger N. (1997). *Size characteristics and ageing of the environmental tobacco smoke.* The Science of the Total Environment. Vol. 196, pp.43-55.

NIH, (1998). *Cigars Health Effects and Trends.* National Institutes of Health; National Cancer Institute Smoking and Tobacco Control Monograph 9.

NTP, (2002). National Toxicology Program. *N-Nitrosornicotine Report on Carcinogens. Tenth Edition;* U.S. Department of Health and Human Services, Public Health Service, National Toxicology Program, December 2002.

OEHHA (Office of Environmental Health Hazard Assessment) (1997). *Health Effects of Exposure to Environmental Tobacco Smoke.* Final Report . California Environmental Protection Agency.

Piade J.J., D'andres D., Sanders E.B. (1999). *Sorption Phenomena of Nicotine and Ethenylpyridine Vapors on Different Materials in a Test Chamber.* Environ. Sci. Technol. Vol. 33, pp. 2046-2052.

Prinn R., Cummond D., Rasmussen R., Simmonds P., Alyea F., Crawford A., Fraser P., Rosen R. (1987). *Atmospheric trends in methylchloroform and the global average for the hydroxyl radical.* Science. Vol. 238, pp. 945-950.

Seinfeld J.H., Pandis S.N. (1998). *Atmospheric Chemistry and Physics: From Air Pollution to Climate Change.* John Wiley and Sons, New York.

Skov H., Hjoth J., Jensen N.R., Restelli G. (1992). *Products and mechanisms of the reactions of the nitrate radical (NO₃) with isoprene, 1,3-butadiene, and 2,3-dimethyl-1,3-butadiene in air.* Atmos. Environ. Vol. 26A, pp. 2771-2783.

Spectrum Chemical Fact Sheet (2003). <http://www.speclab.com/compound/c54115.htm>

Thome F.A., Heavner D.L., Ingebrethsen B.J., Eudy L.W., Green C.R.(1986). *Environmental Tobacco smoke monitoring with an atmospheric pressure chemical ionization mass spectrometer/mass spectrometer coupled to a test chamber*. Proceedings, 79th Annual Meeting of the Air Pollution Control Association. Paper 86-37.6, Pittsburgh, PA.

Trinh V.D. and Huynh C.K. (1989). *Sidestream Tobacco Smoke Constituents in Indoor Air Modeled in an Experimental Chamber-Polycyclic Aromatic Hydrocarbons*. Environmental International. Vol. 15, pp. 57-64.

U.S. EPA (1992). U.S. Environmental Protection Agency. *Respiratory Health Effects of Passive Smoking: Lung Cancer and Other Disorders*. EPA/600/6-90/006F. EPA Office of Research and Development, Washington, DC.

Von Loy M.D., Riley W.J., Daisey J.M., Nazaroff W.W. (2001). *Dynamic Behavior of Semivolatile Organic Compounds in Indoor Air. 2. Nicotine and Phenanthrene with Carpet and Wallboard*. Environ. Sci. Technol. Vol. 35, pp. 560-567.